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Locating and Estimating Air Emissions from Sources of Epichlorohydrin

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Research Triangle Park, NC

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16. ABSTRACT

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents such as this to compile available information on sources and emissions of these substances. This document deals specifically with epichlorohydrin. Its intended audience includes Federal, State and local air pollution personnel and others interested in locating potential emitters of epichlorohydrin in making gross estimates of air emissions therefrom.

This document presents information on 1) the types of sources that may emit epichlorohydrin, 2) process variations and release points that may be expected within these sources, and 3) available emissions information indicating the potential for epichlorohydrin release into the air from each operation.

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U.S. ENVIRONMENTAL PROTECTION AGENCY
Office Of Air And Radiation
Office Of Air Quality Planning And Standards
Research Triangle Park, North Carolina 27711

September 1985

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SECTION 1
PURPOSE OF DOCUMENT

The U. S. Environmental Protection Agency (EPA), States, and local air pollution control agencies are becoming increasingly aware of the presence of substances in the ambient air that may be toxic at certain concentrations. This awareness, in turn, has led to attempts to identify source/receptor relationships for these substances and to develop control programs to regulate emissions. Unfortunately, very little information is available on the ambient air concentrations of these substances or on the sources that may be discharging them to the atmosphere.

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents such as this that compiles available information on sources and emissions of these substances. This document specifically deals with epichlorohydrin. Its intended audience includes Federal, State, and local air pollution personnel and others who are interested in locating potential emitters of epichlorohydrin and making gross estimates of air emissions therefrom.

Because of the limited amounts of data available on epichlorohydrin emissions, and since the configuration of many sources will not be the same as those described herein, this document is best used as a primer to inform air pollution personnel about (1) the types of sources that may emit epichlorohydrin, (2) process variations and release points that may be expected within these sources, and (3) available emissions information indicating the potential for epichlorohydrin to be released into the air from each operation.

The reader is strongly cautioned against using the emissions information contained in this document to try to develop an exact assessment of emissions from any particular facility. Since insufficient data are available to develop statistical estimates of the accuracy of these emission factors, no estimate can be made of the error that could result if these factors were used to calculate emissions from any given facility. It is possible, in some extreme cases, that orders-of-magnitude differences could result between actual and calculated emissions, depending on differences in source configurations, control equipment, and operating practices. Thus, in situations where an accurate assessment of epichlorohydrin emissions is necessary, source-specific information should be obtained to confirm the existence of particular emitting operations, the types and effectiveness of control measures, and the impact of operating practices. A source test and/or material balance should be considered as the best means to determine air emissions directly from an operation.

SECTION 2
OVERVIEW OF DOCUMENT CONTENTS

As noted in Section 1, the purpose of this document is to assist Federal, State, and local air pollution agencies and others who are interested in locating potential air emitters of epichlorohydrin and making gross estimates of air emissions therefrom. Because of the limited background data available, the information summarized in this document does not and should not be assumed to represent the source configuration or emissions associated with any particular facility.

This section provides an overview of the contents of this document. It briefly outlines the nature, extent, and format of the material presented in the remaining sections of this report.

Section 3 of this document provides a brief summary of the physical and chemical characteristics of epichlorohydrin, its commonly occurring forms, and an overview of its production and uses. A table summarizes the quantities of epichlorohydrin consumed in various end uses in the United States. This background section may be useful to someone who needs to develop a general perspective on the nature of the substance and where it is manufactured and consumed.

The fourth and fifth sections of this document focus on major industrial source categories that may discharge epichlorohydrin air emissions. Section 4 discusses the production of epichlorohydrin and Section 5 discusses the use of epichlorohydrin as an industrial feedstock in the production of synthetic glycerin and epoxy resins. For each major industrial source category described in Sections 4 and 5, example process descriptions and flow diagrams are given, potential emission points are

identified, and available emission factor estimates are presented that show the potential for epichlorohydrin emissions before and after controls employed by industry. Individual companies are named that are reported to be involved with either the production and/or use of epichlorohydrin, based on industry contacts and available trade publications. Section 6 contains information on possible releases of epichlorohydrin to air from the use of materials containing trace epichlorohydrin levels.

The final section of this document summarizes available procedures for source sampling and analysis of epichlorohydrin. Details are not prescribed nor is any EPA endorsement given or implied to any of these sampling and analysis procedures. At this time, EPA has generally not evaluated these methods. Consequently, this document merely provides an overview of applicable source sampling procedures, citing references for those interested in conducting source tests.

This document does not contain any discussion of health or other environmental effects of epichlorohydrin, nor does it include any discussion of ambient air levels or ambient air monitoring techniques.

Comments on the contents and usefulness of this document are welcomed, as is any information on process descriptions, operating practices, control measures, and emissions information that would enable EPA to improve its contents. All comments should be sent to:

Chief, Source Analysis Section (MD-14)
Air Management Technology Branch
U. S. Environmental Protection Agency
Research Triangle Park, N. C. 27711

SECTION 3
BACKGROUND

NATURE OF POLLUTANT

Epichlorohydrin is a colorless, free-flowing, highly reactive liquid. Its irritating odor has been likened to that of chloroform or garlic. It is both volatile and flammable. It is soluble in most organic solvents and forms azeotropes with many organic liquids. It is slightly soluble in petroleum hydrocarbons and in water. Because of an asymmetric carbon atom in the molecule, epichlorohydrin exists as an isomeric mixture with equal amounts of the dextro- and levorotary forms. Synonyms and trade names for epichlorohydrin are given in Table 1; physical and chemical properties are summarized in Table 2. The Chemical Abstracts Service (CAS) registry number for epichlorohydrin is 106-89-8.[1,2]

Epichlorohydrin is not persistent in the environment, hydrolyzing in several weeks. Its atmospheric residence time, the estimated time in days required for a given quantity to be reduced to 1/e (37 percent) of its original value, is 5.8.[3] At 20°C (68°F), its half-life in distilled water is 8.0 days; in 3 percent sodium chloride, the half-life is 5.3 days. Epichlorohydrin also participates in free-radical photochemical reactions.[4]

OVERVIEW OF PRODUCTION AND USE

Epichlorohydrin is produced commercially in the United States by chlorohydrating allyl chloride into isomeric glycerol dichlorohydrins, which are then dehydrochlorinated with alkali to form crude epichlorohydrin. Crude epichlorohydrin can be used directly for the production of synthetic glycerin or refined for other uses.[2]

TABLE 1. SYNONYMS AND TRADE NAMES FOR EPICHLOROHYDRIN[2]

1-chloro-2,3-epoxypropane	glycidyl chloride
3-chloro-1,2-epoxypropane	(chloromethyl)oxirane
(chloromethyl)ethylene oxide	3-chloro-1,2-propylene oxide
2-(chloromethyl) oxirane	α-epichlorohydrin
chloropropylene oxide	D,L-α-epichlorohydrin
α-chloropropylene oxide	SKEKhG
3-chloropropene 1,2-oxide	1,2-epoxy-3-chloropropane
2-chloromethyl oxirane	2,3-epoxypropyl chloride
ECH	glycerol epichlorohydrin

TABLE 2. SUMMARY OF THE PHYSICAL AND CHEMICAL PROPERTIES OF EPICHLOROHYDRIN[2]

Molecular Formula	$CH_2 \text{---} CH\text{-}CH_2Cl$ (epoxide ring: O bridging the two CH groups)
Molecular Weight	92.53
Elemental Composition	C = 38.94% H = 5.45% Cl = 38.32% O = 17.29%
Physical Properties	
Melting Point	-48.0°C
Freezing Point	-57°C
Boiling Point	116°C
Density (g/ml, 20°C)	d_4^{20} 1.1812
Specific Gravity (20/20°C)	1.181
Vapor Pressure (16.6°C)	10 mmHg
(30°C)	22 mmHg
Concentration in Saturated Air (760 mmHG, 25°C)	1.7%
Coefficient of Thermal Expansion at 68°F	0.000577 per °F
Solubility	
Water (10°C)	6.52%
Water (20°C)	6.58%
Pounds per Gallon (68°F)	9.85
Flash Point (Tag open cup)	41°C
(Tag closed cup)	31°C
Autoignition Temperature	416°C
Latent Heat of Vaporization (calc.)	9060 cal/mole at the b.p.
Odor Threshold in Air	10 ppm
Surface Tension (20°C)	37.00 dynes/cm
Heat of Combustion	4524.4 cal/gm
Liquid Viscosity (25°C)	0.0103 poise
Refractive Index (25°C)	n_D 1.4358
1 ppm at 25°C & 760 mmHg equivalent to	3.78 mg/m^3
1 mg/l at 25°C & 760 mmHg equivalent to	265 ppm
Heat Capacity (25°C)	31.5 cal/mol°C
(100°C)	40.0 cal/mol°C
Heat of Formation (25°C)	-35.6 Kcal/mol
Explosive Limits (volume % in air)	3.8-21.0
Heat of Fusion (25°C)	2,500 cal/mol

Several alternative methods are being developed for producing epichlorohydrin, but as of 1983 none are yet approaching commercial application.[5] These methods include:

- Epoxidation of allyl chloride with:
  --peracids;
  --perborates;
  --tert-butyl hydroperoxide in the presence of vanadium, tungsten, or molybdenum catalysts;
  --α-phenylethyl hydroperoxide;
  --air or oxygen in systems which include aluminum-silver oxide ($Al-Ag_2O$) or dimethyl phthalate-acetaldehyde.

- Chlorination of allyl alcohol to dichlorohydrins.

- Hydrochlorination of glycerol to chlorohydrins.

- Chlorination of acrolein to 2,3-dichloropropionaldehyde and reduction with sec-butyl alcohol to 2,3-dichlorohydrin.

As of 1984, only two companies -- Dow Chemical Company, Freeport, TX, and Shell Chemical Company, Norco, LA -- produced epichlorohydrin. (Crude epichlorohydrin from Shell Oil's Norco plant is finished at Shell's Deer Park, TX plant.) Two epoxy resin manufacturers -- Union Carbide and the Plastics and Additives Division of Ciba-Geigy -- have had the capacity to produce epichlorohydrin from purchased allyl chloride, but as of 1975 had not done so for several years.[6-9]

Domestic consumption of epichlorohydrin for 1984 is summarized in Table 3.[10] Both quantity and percent of total epichlorohydrin consumption are given. Crude epichlorohydrin may be used directly for the production of synthetic glycerin or it may be refined for other uses. In 1982, more than 90 percent of the total U. S. production of unmodified epoxy resins was

TABLE 3. ESTIMATED DOMESTIC CONSUMPTION OF EPICHLOROHYDRIN IN 1984 [10]

Product	Quantity Gg (10^6 lb)	% Total Domestic Production of Crude Epichlorohydrin	Major Uses
Epoxy Resins	77-79 (172-175)	56	Surface coatings, laminates/comosites, castings/ molding, flooring.
Bisphenol A (DGEBPA)			
Aliphatic			
Polyether			
Epoxy Novolac			Adhesives.
Phenoxy Epoxy and Other Epoxy			
Synthetic Glycerin	39-41 (87-90)	29	Ingredient for food/beverage, cosmetics, drugs; humectant in tobacco; plasterizer for cellophane and reactant in alkyd resin, urethane polymers, triacetin explosives production.
Wet-Strength Resins	5-7 (10-15)	5	Paper industry, for paper sizing.
Water Treatment Polymers	6 (12)	4	Water clarification, waste water treatment flocculating agents.
Elastomers	3-4 (7-9)	3	Seals, gaskets, jackets for wire and cable, hoses, belts, rubberized fabrics.
Anion Exchange Resins	<0.5 (<1)	0.2	
Alkyl Glyceryl Ether Sulfonates	1-2 (3-5)	1	Surfactants; shampoos, liquid detergents.
Glycidyl Ethers	1 (3)	1	Reactive dilutants for epoxy resins.
Glycidyl Esters	<0.5 (<1)	0.2	
Fyrol FR-2	1 (2)	0.6	Flame retardant.
Total (approximate)	140 (311)	100	

produced from refined epichlorohydrin. Epoxy resins are cured either by reaction with a cross-linking agent (hardener) or by self-polymerization with the aid of a catalyst. Epoxies are used in reinforced plastics, casting, potting, encapsulation, molding compounds, protective coatings, and adhesives.[11]

Other uses for epichlorohydrin include the production of epichlorohydrin elastomers, glycidyl ethers, wet-strength resins, water treatment resins, surfactants, solvents, adhesives, inks and dyes, asphalt improvers, corrosion inhibitors, fumigants, flame retardents, sterilizing agents, and pesticides. About 5 percent of the epichlorohydrin produced in the United States is exported to other countries.[11]

All emissions from the production and use of epichlorohydrin can be broadly related to process vents, storage operations, and fugitive losses from pumps, valves, flanges, etc.

According to a study based mainly on engineering calculations and assumptions about the composition of exhaust gas streams, fugitive emissions are the largest source of epichlorohydrin, accounting for 84 percent of the total annual epichlorohydrin emissions. Storage losses account for 12 percent and process vents only 4 percent. (This distribution of emissions will vary widely at individual facilities.) Fugitive emissions are the largest source of epichlorohydrin emissions because of the numerous pumps, valves, etc., in most plants and because most other sources, particularly process discharges, are generally well controlled. It should be noted, however, that fugitive emissions may be less important in batch operations, such as those producing wet strength resins, elastomers, and surfactants, because epichlorohydrin is not flowing through the process components continuously, as was assumed in the study.[12]

There are no known uses of epichlorohydrin as a solvent; hence, no solvent-related emissions would be expected from dispersed end use applications as are common with many other organic chemicals.

Some potential exists for volatile substances, including epichlorohydrin, to be emitted from waste treatment, storage, and handling facilities. Reference 13 provides general theoretical models for estimating volatile substance emissions from a number of generic kinds of waste handling operations, including surface impoundments, landfills, land farming (land treatment) operations, wastewater treatment systems, and drum storage/handling processes. Since no test data were available on epichlorohydrin emissions from any of these operations at the time of publication, no further discussion is presented in this document. If such a facility is known to handle epichlorohydrin, the potential for some air emissions should be considered.

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SECTION 4
EMISSIONS FROM EPICHLOROHYDRIN PRODUCTION

Epichlorohydrin can be released to the atmosphere both during its production and during its consumption as a raw material in other manufacturing processes. This section details the production of epichlorohydrin and the emission factors associated with that production. Manufacturing processes which use epichlorohydrin as a feedstock are described in Section 5.

EPICHLOROHYDRIN PRODUCTION

Process Description

Several processes have been developed for producing epichlorohydrin. A generalized process is described here, showing the basic operations involved. Figure 1 shows a process flow diagram of this generalized process; Table 4 describes the streams and vents illustrated in Figure 1.[1] Shell Oil has indicated that their crude epichlorohydrin production process differs from the generic epichlorohydrin process shown in Figure 1; however, details on how it differs were not provided.[2] The subheadings in the following text correspond to the major component operations involved in epichlorohydrin production. Process variations discussed are those known to be practiced by various manufacturers.

Allyl Chloride Production[1]--

Allyl chloride is derived from dry propylene by direct chlorination in a high-temperature [~500°C (932°F)] gas phase reactor according to the following reaction:

Note: The numbers in this figure refer to process streams, as discussed in the text. Letters designate process vents. Heavy lines represent product flow through the process.

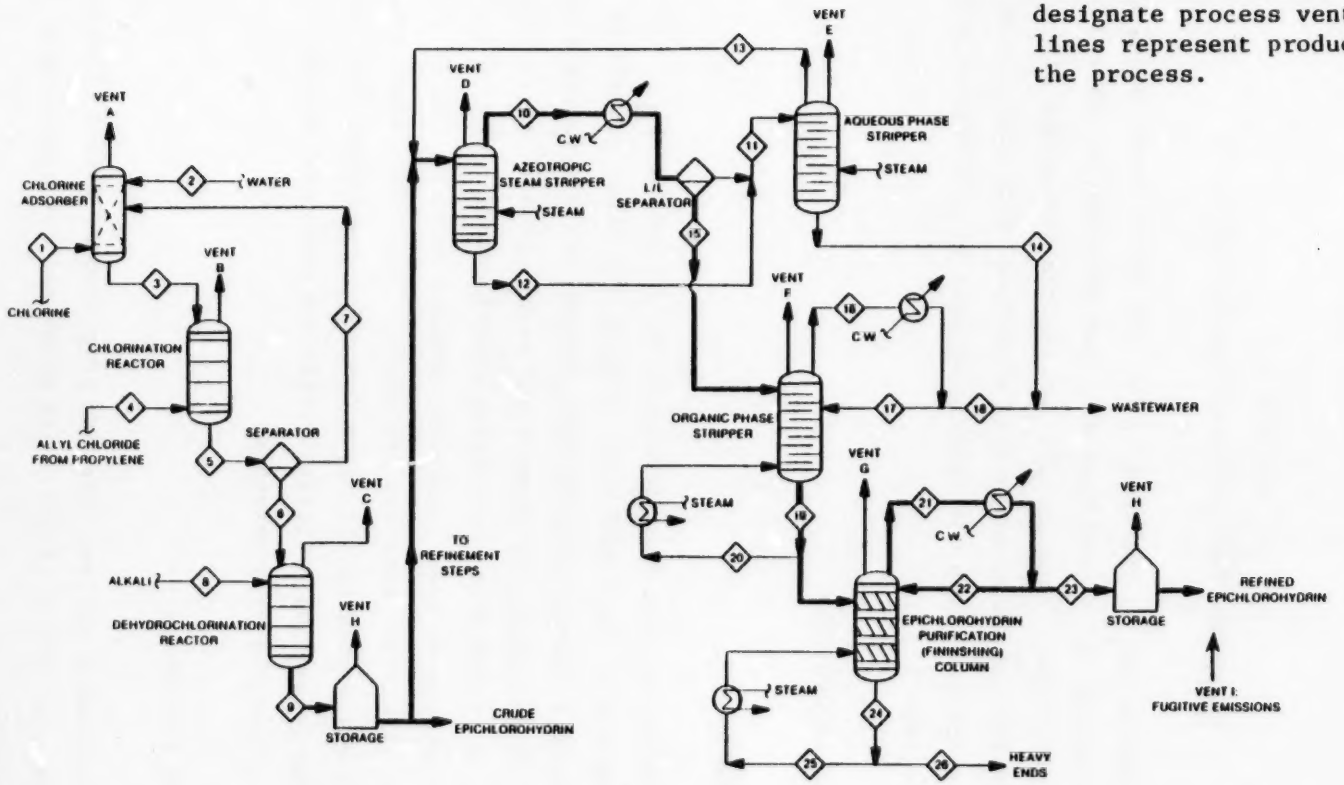


Figure 1. Basic Operations that May Be Used in the Production of Epichlorohydrin from Allyl Chloride

TABLE 4. DESCRIPTION OF STREAMS AND VENTS ILLUSTRATED IN FIGURE 1 FOR THE PRODUCTION OF EPICHLOROHYDRIN

Code Number	Description
Stream	
1	Chlorine feed
2	Water feed
3	Dilute hypochlorous acid
4	Allyl chloride feed
5	Dehydrochlorination reactor product
6	Separator underflow (3-5% dichlorohydrin)
7	Recycle to chlorine absorber (optional)
8	Alkali feed (sodium or calcium hydroxide or carbonate)
9	Dehydrochlorination reactor product
10	Azeotropic stream stripper overhead (26% epichlorohydrin/water azeotrope)
11	Liquid phase from azeotropic stripper combined with stripper bottoms (12)
12	Azeotropic steam stripper bottoms
13	Recycle to azeotropic steam stripper
14	Aqueous phase stripper bottoms
15	Organic phase from azeotrope
16	Overhead from organic phase stripper
17	Overhead recycle to organic phase stripper
18	Separator overhead condensate to wastewater
19	Organic phase stripper bottoms
20	Bottoms recycle to organic phase stripper
21	Purification column product
22	Overhead recycle to purification column
23	Final product epichlorohydrin
24	Purification column bottom
25	Bottoms recycle to purification column
26	Purification column bottoms to wastewater
Vent	
A	Chlorine absorber vent
B	Chlorination reactor vent
C	Dehydrochlorination reactor vent
D	Azeotropic steam stripper vent
E	Aqueous phase stripper vent
F	Organic phase stripper vent
G	Purification column vent
H	Storage tanks vents
I	Fugitive emissions, including valves, flanges, pump seals, etc.

$$CH_2{=}CH{-}CH_3 + Cl_2 \longrightarrow CH_2{=}CH{-}CH_2Cl + HCl$$

Propylene — Chlorine — Allyl chloride — Hydrochloric acid

The crude allyl chloride is fractionated and purified in several columns. As Stream 4 it is fed to the chlorination reactor.

Hypochlorous Acid Production[1]--

Hypochlorous acid is produced from chlorine (Stream 1) and water (Stream 2) in a packed tower chlorine absorber unit by the following reaction:

$$Cl_2 + H_2O \longrightarrow HClO + HCl$$

Chlorine — Water — Hypochlorous acid — Hydrochloric acid

The absorber may be eliminated entirely by feeding gaseous chlorine and water directly into the chlorination reactor (discussed next) along with the allyl chloride.

Dichlorohydrin Production[1]--

Hypochlorous acid (Stream 3) and allyl chloride (Stream 4) are combined in a chlorination reactor. The chlorination occurs at atmospheric pressure in the liquid phase:

$$2\ CH_2{=}CH{-}CH_2Cl + 2\ HClO \longrightarrow CH_2Cl{-}CHCl{-}CH_2OH + CH_2Cl{-}CHOH{-}CH_2Cl$$

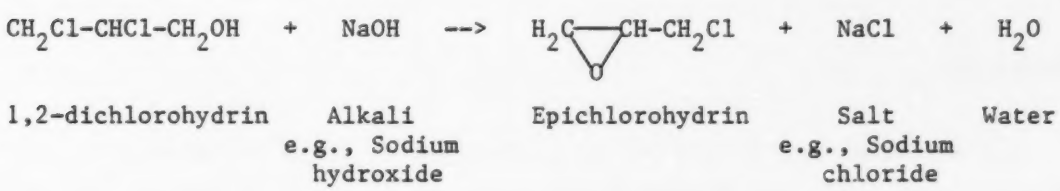
Allyl chloride — Hypochlorous acid — 1,2-dichlorohydrin (70%) — 1,3-dichlorohydrin (30%)

The reactor product stream (Stream 5) is sent to a separator. The separator underflow (Stream 6), which contains about 3 to 5 percent dichlorohydrin

isomers, is routed to the dehydrochlorination reactor. Recycle of the aqueous separator overflow (Stream 7) to the chlorination absorber is optional.

Epichlorohydrin Production--

An alkali (Stream 8) is added to Stream 6 in the dehydrochlorination reactor. The alkali can be sodium (or calcium) hydroxide or sodium (or calcium) carbonate. Use of a carbonate alkali greatly increases emissions from the process because the large amount of CO_2 produced acts as a sweep gas.[1] A difference of opinion exists in the literature as to whether the choice of alkali is a process option or a control option. The dichlorohydrins undergo dehydrochlorination and epoxidation according to the following reaction:



An excess of alkali drives the reaction to completion. The crude epichlorohydrin product stream (Stream 9) from the reactor contains 3 to 5 percent epichlorohydrin, other reaction products, and water.[1,3] The crude epichlorohydrin may be used directly in the production of glycerin or it may be refined for use in other manufacturing processes.

Purification and Recovery of Epichlorohydrin[1]--

The crude epichlorohydrin stream (Stream 9) is purified first by azeotropic steam stripping. The overhead from the stripper (Stream 10), an epichlorohydrin/water azeotrope with 26 percent water, is then separated in a liquid/liquid (1/1) separator into aqueous and organic phases. The aqueous phase from the 1/1 separator is combined with the bottoms from the

azeotropic steam stripper (Stream 12) and sent (Stream 11) to an aqueous phase steam stripper. The overhead from the aqueous phase stripper (Stream 13) contains some epichlorohydrin and is therefore recycled to the azeotropic steam stripper. The bottoms from the aqueous phase stripper is a wastewater stream (Stream 14). One producer does not use an aqueous phase stripper and considers Stream 11 to be a waste stream.[4]

A portion of the bottoms from the organic phase stripper (Stream 19) is heated in a boiler and recycled to the stripper (Stream 20). The remainder of the bottoms is sent to the final purification column where purified epichlorohydrin is fractionated, removed overhead, and condensed (Stream 21). A portion of the product stream (22) and a portion of the bottoms stream (Stream 25) are recycled to the column. The remainder of the product stream (Stream 23) is the final product epichlorohydrin. The remainder of the bottoms stream (Stream 26) is a wastewater stream.

Emissions

The preliminary processes for production of allyl chloride, hypochlorous acid, and dichlorohydrin involve no epichlorohydrin. Hence, no epichlorohydrin is emitted from either vents A or B or from any tanks, valves, pumps, etc., used to store or transport materials in any of the operations associated with Streams 1 through 8 in Figure 1.

Most of the emissions from today's epichlorohydrin production facilities are fugitive or storage losses.[5] Fugitive losses include those from the numerous valves, flanges, pump seals, sampling ports, etc., found in a production plant. Fugitive emissions dominate because they are numerous, and because other sources are fewer and/or well controlled.

Many of the chemicals involved in the epichlorohydrin production process are flammable and/or toxic; therefore, equipment is likely to be well maintained for safety reasons.[1] One producer encloses all process and

tank sampling points in domes connected to a vacuum system. Area monitors detect leaks or spills of any chlorinated hydrocarbon. The detection limit for the monitors is less than 0.1 ppm. In addition, personnel monitoring and sampling of different areas of the plant are part of the industrial hygiene program.[6]

Table 5 enumerates the types of fugitive epichlorohydrin emission sources in plants which produce and/or finish epichlorohydrin. These sources and the various control methods used to minimize emissions from them are described in Reference 7.

In 1984, with the exception of one internal floating roof tank, all epichlorohydrin at the production and/or finishing facilities was stored in fixed roof tanks.[6,8,9] One producer has the epichlorohydrin finishing facility (refinery) separate from the production facility; therefore, crude epichlorohydrin is shipped by boat from production to finishing.[10]

Process vent emissions constitute only a small fraction of the total controlled epichlorohydrin emissions from a modern production facility. Little information is available concerning the process conditions which affect emissions of epichlorohydrin from process vents. No information is available on how (or whether) process upsets or startups affect these emissions.

The vent gas from the dehydrochlorination reactor (Vent C) is known to contain some epichlorohydrin. This vent can be the largest gaseous emission source in the plant, but is not necessarily the largest source of epichlorohydrin emissions. The composition of the vent stream depends on reactor design, operating conditions, and the type of alkali used. If carbonate is used as the alkali source, the large volume of carbon dioxide formed entrains a large volume of epichlorohydrin vapors with it as it exits the vent. In this case, carbon adsorption or incineration is used to control the vent VOC emissions. However, hydroxide alkali may be used instead to reduce greatly the vapors from this vent.[1]

TABLE 5. SOURCES OF FUGITIVE EPICHLOROHYDRIN EMISSIONS FROM EQUIPMENT LEAKS IN EPICHLOROHYDRIN PRODUCTION/FINISHING FACILITIES[6,8,9,a]

Equipment Type		Number of Components in Epichlorohydrin Service (weight percent epichlorohydrin)					
		Less than 5 Percent	5-10 Percent	11-25 Percent	26-75 Percent	76-99 Percent	Greater than 99 Percent
Pump Seals	Packed	-	-	-	-	-	-
	Mechanical	24[b]	2	-	2	10	6
	Double Mechanical	7	-	1	2	5	4
Compressors		-	2	-	-	-	-
Flanges		1,791	104	245	340	1,697	580
Valves	Gas[c]	86	3	10	32	27	29
	Liquid	479	28	54	100	440	196
All Pressure Relief Devices	Gas[c]	5	-	2	7	-	5
	Liquid	5	-	-	-	3	2
Sample Connections	Gas	-	-	-	-	-	-
	Liquid	16	2	1	5	10	5
Open Ended Lines[d] (e.g., purge, vent)	Gas	10	-	11	20	10	10
	Liquid	137	4	20	50	79	40

[a]These numbers are component totals for the two U. S. epichlorohydrin producers, Dow Chemical and Shell Oil, and include those components at Shell's Deer Park, TX, epichlorohydrin finishing plant. These counts are not representative of any particular production facility.

[b]As an example of how to use this table, this number means that there are 24 mechanical seals serving streams containing less than 5 weight percent epichlorohydrin. Emissions can be calculated by multiplying emission factors for each type of device (e.g., from Reference 7) by the device count and adjusting for the weight percent epichlorohydrin in each stream.

[c]Conditions existing in the pipe during normal operation.

[d]Lines closed during normal operation that would be used during maintenance operations. Dow Chemical indicates all of its open ended lines are kept blinded or plugged.

The vent from the azeotropic steam stripper (Vent D) is not a large source of epichlorohydrin emissions. Either a thermal oxidizer or a wet scrubber can be used for control of emissions from this point. Organic emissions from the aqueous phase stripper (Vent E) can be controlled by incineration, carbon adsorption, or wet scrubbing.

The vent from the organic phase stripper (Vent F) can be a large source of VOC emissions. The percentage of epichlorohydrin in this stream is not known. The vent from the purification column (Vent G) releases only a small quantity of VOC emissions, but the stream consists primarily of epichlorohydrin. Emissions from these vents can be controlled by flares, incineration, scrubbing, carbon adsorption, or the use of refrigerated vent condensers.

One producer routes all process emissions to a thermal oxidizer-NaOH scrubber unit. Control efficiency is reported by the company to be 99.99+ percent. No epichlorohydrin has been detected from this source. Assuming a 0.1 ppm detection limit for the method used, calculations by the producer indicate an epichlorohydrin emission rate less than 79 kg/yr if the facility is operated at full capacity.[6]

Another producer apparently routes all process emissions from production to a single stack controlled by a vent condenser. The producer reports zero epichlorohydrin emissions from this source.[9] Emissions from the corresponding separate finishing operations (1 percent epichlorohydrin) are routed to incinerators rated as 99.99 percent efficient.[8] The stripper bottoms stream (Stream 26) is known to contain some epichlorohydrin. However, this stream is treated by hydrolysis and biotreatment before disposal. The amount of epichlorohydrin which escapes from this source is not known.

Emission Factors

Table 6 presents available emission factor data for epichlorohydrin production. This table represents industrywide totals.

TABLE 6. EMISSION FACTORS FOR THE RELEASE OF EPICHLOROHYDRIN FROM EPICHLOROHYDRIN PRODUCTION

Source	Emission Factor[a] (g/kg)	% Total Emission
Process Vents	0.00047[b,f]	0.06[b]
Storage Facilities[c]	0.15	19.9
Fugitive Sources[d]	0.62	80.0
TOTAL[e]	0.78	100.0

[a]Grams of epichlorohydrin emitted per kilogram of epichlorohydrin produced. Based on a nationwide annual production rate of 191 Gg (420×10^6 lb) epichlorohydrin[11] and nationwide emission totals from Reference 5. As such, these factors do not necessarily represent emission rates from any particular facility.

[b]These factors represent epichlorohydrin emissions after controls (thermal oxidizers/NaOH scrubbers, vent condensers, and incinerators) reportedly effecting 99.99 percent removal.

[c]Includes storage tanks (mainly fixed roof), transfer operations, etc. Storage emissions from glycerin manufacture are also included.

[d]Includes valves, flanges, pump seals, sampling ports, etc. Emission factors are approximated from average VOC emission factors for SOCMI process components and represent a relatively uncontrolled facility where no significant leak detection and repair programs are in place to limit fugitive emissions. One manufacturer[6] uses area monitors and employee exposure monitors to detect spills or leaks and has equipped all process and tank sampling points with an enclosed dome connected to a block vacuum system, which directs the epichlorohydrin vapors to a thermal oxidizer. No estimate is available of the the effectiveness of these measures.

[e]Independent numerical roundoff may affect totals.

[f]Reference 12 indicated that epichlorohydrin emissions to air from reactor vent gas were 1.5 g/kg epichlorohydrin produced. The reference does not indicate whether this situation is for controlled or uncontrolled emissions. Besides the reactor vent gas, no other epichlorohydrin emission sources were identified.

Data are not available to describe accurately the emissions from all operations associated with epichlorohydrin production. When inventorying emissions of epichlorohydrin from such facilities, source-specific information should be obtained to determine the existence of emitting operations, control equipment, and emission levels.

Source Locations

As of 1984, only two companies are producing epichlorohydrin: Shell Oil Company in Norco, LA, and Dow Chemical Company in Freeport, TX. Crude epichlorohydrin from the Shell facility is finished (refined) at Shell's facility in Deer Park, TX. Of the epichlorohydrin finished at the Deer Park Facility, some is used directly there for the production of epoxy resins and some is sold as finished epichlorohydrin.[2,6,9]

INADVERTENT PRODUCTION OF EPICHLOROHYDRIN IN OTHER INDUSTRIAL PROCESSES[3]

Epichlorohydrin can be produced as a byproduct during the manufacture of a number of other chemicals. Therefore, it can be emitted not only from processes which manufacture these other chemicals, but also (because it is a contaminant in these chemicals) from processes which use these chemicals as feedstock and from other uses (solvent, etc.) of these chemicals. No information is available on the amount of epichlorohydrin emissions from this source.

The most likely precursors of epichlorohydrin are:

- Allyl Chloride
- 2,3 - Dichloropropene,
- 1,3 - Dichloro -2-propanol,
- 1,3 - Dichloropropene,
- Tris (Dichloropropyl) Phosphate, and
- Glycerin.

REFERENCES FOR SECTION 4

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4. Hydroscience, Inc. Trip Report: Dow Chemical Company, Freeport, TX. 1978. As cited in Engineering Analysis of Epichlorohydrin Production Process, Preliminary Document. (Prepared for U. S. Environmental Protection Agency, Contract No. 68-02-3171.) Radian Corporation, McLean, VA. September 1981.

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7. VOC Fugitive Emissions in Synthetic Organic Chemicals Manufacturing Industry--Background Information for Proposed Standards. EPA-450/3-80-033b. U. S. Environmental Protection Agency. Research Triangle Park, NC. November 1980.

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11. Chemical Products Synopsis. Manville Chemical Products. Cortland, NY. December 1982.

12. Assessment of Epichlorohydrin Uses, Occupational Exposure, and Releases. Dynamac Corporation, Rockville, MD. Prepared for the Office of Toxic Substances, U. S. Environmental Protection Agency, Washington, DC. Prepared under EPA Contract No. 68-02-3952. July 1984.

SECTION 5

EMISSIONS FROM INDUSTRIES WHICH USE EPICHLOROHYDRIN AS A FEEDSTOCK

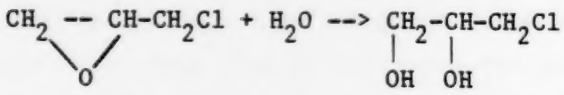
About 85 percent of the epichlorohydrin produced in the United States is used as a feedstock in the production of synthetic glycerin and epoxy resins. These production processes, along with the epichlorohydrin emissions associated with them, are described in this section. Other uses of epichlorohydrin include the manufacture of elastomers, glycidyl ethers, wet strength resins, surfactants, water treatment resins, and other products. (See Table 3). Because of inadequate information, these other products are not discussed in this section. The locations of a few known producers of these other products are listed at the end of the section.

PRODUCTION OF SYNTHETIC GLYCERIN

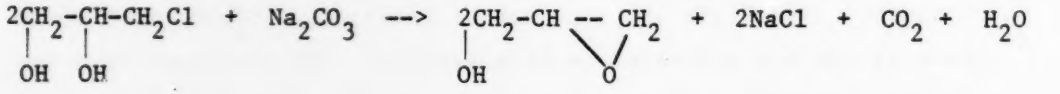
Synthetic glycerin is a chemical intermediate used in the production of materials such as alkyd resins (for paints), cellophane and meat casings, tobacco (including triacetin), explosives and other military products, drugs, toothpaste, cosmetics, monoglycerides and foods, and urethane foams. The largest single use for synthetic glycerin is in the production of tobacco materials, which consumes 18 percent of all synthetic glycerin generated. Synthetic glycerin is in direct competition for use with natural glycerin. In many cases synthetic glycerin is preferred because of its lower moisture content. Synthetic glycerin has been used exclusively for polyols and urethane foams because of its lower moisture content.[1]

Process Description

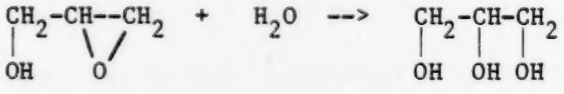
Crude epichlorohydrin is piped directly from the dehydrochlorination reactor of the epichlorohydrin production plant (Stream 9 of Figure 1). Without further purification, the crude epichlorohydrin is blended with a large volume of dilute aqueous sodium carbonate, then heated in a hydrolyzer to convert epichlorohydrin to glycerin by the following reaction sequence.[2]



Epichlorohydrin Water α-monochlorohydrin

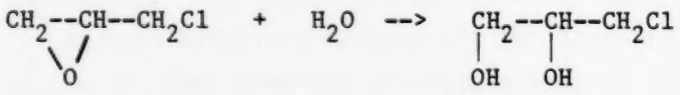


α-monochloro-hydrin Sodium carbonate Glycidol Sodium chloride Carbon dioxide Water

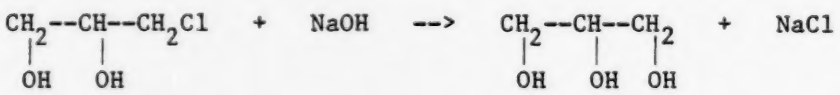


Glycidol Water Glycerin

Another reaction sequence which can be used involves the addition of aqueous sodium hydroxide.[3]



Epichlorohydrin Water α-monochlorohydrin



α-monochlorohydrin Sodium hydroxide Glycerin Sodium chloride

No information is available concerning the predominance of either of these sequences or concerning how significantly the choice of sequence affects emissions from the process. Further description here of the process assumes the first sequence.

A generalized flow diagram for the production of synthetic glycerin from crude epichlorohydrin is given in Figure 2. The production stream from the hydrolyzer contains about 20 to 25 percent glycerin and 10 to 15 percent salt. Excess sodium carbonate is neutralized with hydrochloric acid; the carbon dioxide thus generated is captured in a carbon dioxide adsorber with dilute sodium hydroxide as the absorbing liquid. Aqueous sodium carbonate formed in the absorber is routed to the sodium carbonate storage area for use in the hydrolyzer.[2]

Multiple-effect evaporators remove some of the water from the product stream, thus causing the salt to crystallize. The resulting raw glycerin/salt/water slurry is centrifuged to remove the salt crystals; a water rinse in the centrifuge washes residual glycerin from the salt crystals. The centrifuged product stream at this point is about 45 percent glycerin. A repeat of the evaporation and centrifugation steps raises the glycerin percentage in the solution to about 85 percent.[2]

Finishing involves distillation, solvent extraction (with acetone solvent) and, as the final step, activated carbon adsorption to remove trace impurities and color bodies.[2]

Emission Factors

Most vents release inert gases and water vapor with no significant VOC of any kind. The vent stream from the CO_2 absorber is routed to the thermal oxidizer/NaOH scrubber unit in the epichlorohydrin section. This unit has a 99.99+ control efficiency.[4] There is no evidence of emissions of epichlorohydrin from the process during upsets, i.e., system malfunctions.[3]

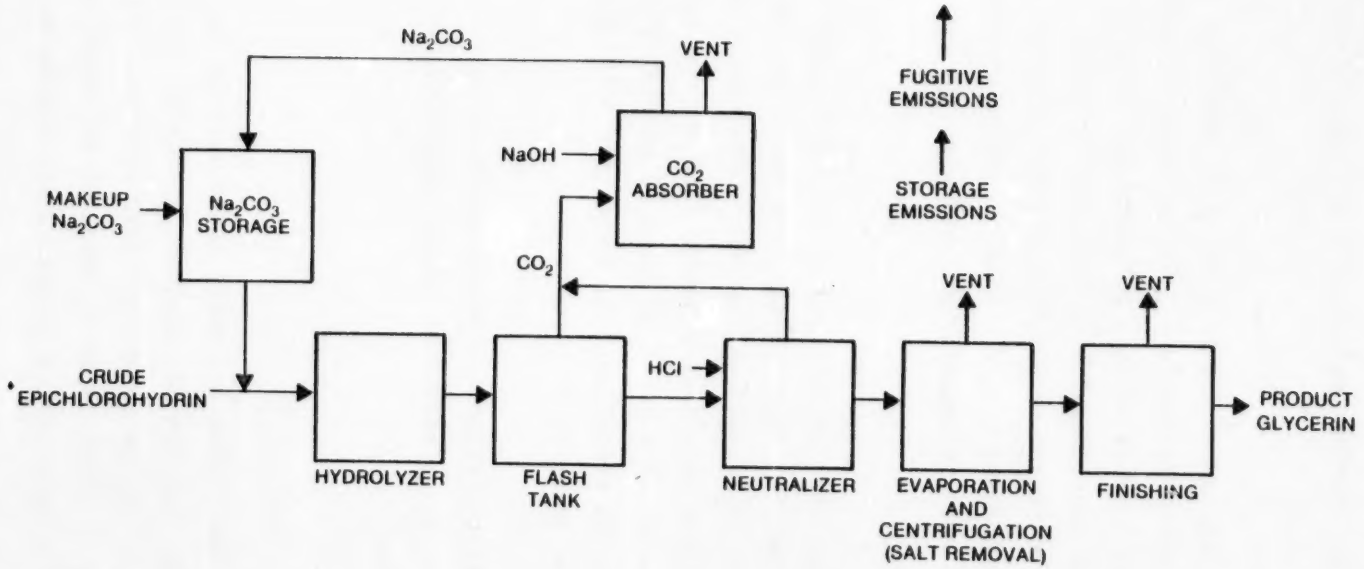


Figure 2. Basic operations that may be used in the production of synthetic glycerin from epichlorohydrin.

Glycerin production plants must be well maintained to protect personnel from the highly flammable and toxic chemicals involved in the process.[2] All process and tank sampling ports are enclosed in domes connected to a vacuum system. Area monitors detect leaks or spills of any chlorinated hydrocarbons. Personnel monitors and sampling of different areas of the plant are part of an industrial hygiene program.[4]

Source Locations

Recently, Dow Chemical Company, Freeport, TX, has been the only U.S. producer of glycerin from epichlorohydrin.[4,5]

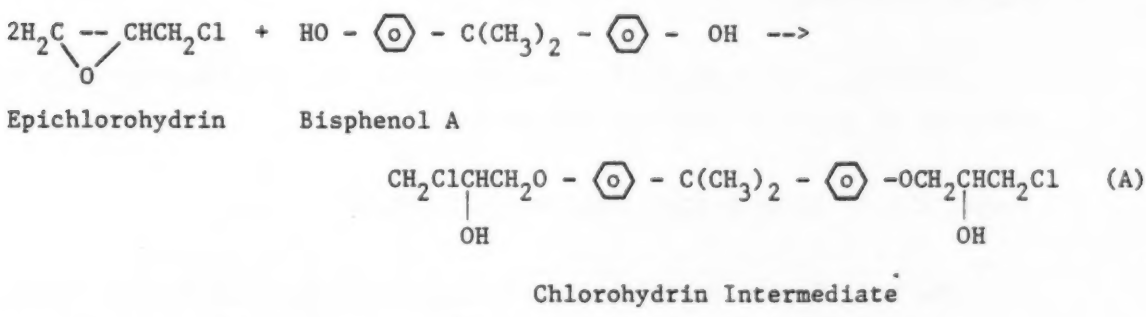
PRODUCTION OF EPOXY RESINS (CONTINUOUS PROCESS)

The term "epoxy resin" applies to polymeric materials which contain epoxide groups. A curing or hardening agent converts the resin to a thermoset material. More than 90 percent of the total U.S. production of unmodified epoxy resins is produced by reacting epichlorohydrin with bisphenol A [2,2-di(4-hydroxyphenyl) propane]. These resins, known as diglycidyl ethers of bisphenol A, may vary from low-viscosity liquids to high-melting solids, depending on the ratio of epichlorohydrin to bisphenol A. Production of the liquids requires 0.68 lb epichlorohydrin per pound of product; production of solids requires 0.47 lb/lb.[3]

Other active hydrogen compounds are also reacted with epichlorohydrin to form epoxy resins: epoxy novolac resins require 0.73 lb epichlorohydrin per pound of product and phenoxy resins require 0.4 lb/lb.[3] Because of the small volumes involved, epoxy and other resins are more likely to be made in batches rather than by continuous processes.[6] They are discussed in the next subsection along with other products made in batches.

Process Description

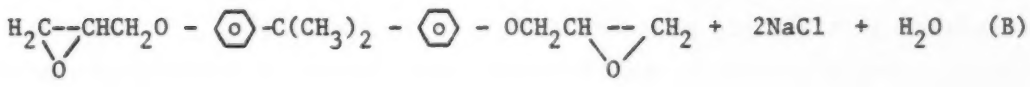
Figure 3 is a generalized flow diagram for the continuous production of epoxy resins from epichlorohydrin and bisphenol A. Raw materials are contacted in a reactor to form an organic resin solution product and an aqueous brine by-product. Available reaction data indicate that the resin forms by the following reactions.[3]



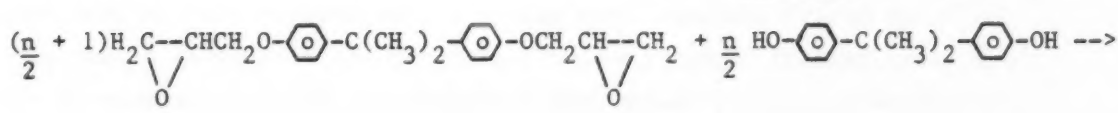
Epichlorohydrin Bisphenol A

Chlorohydrin Intermediate (A)

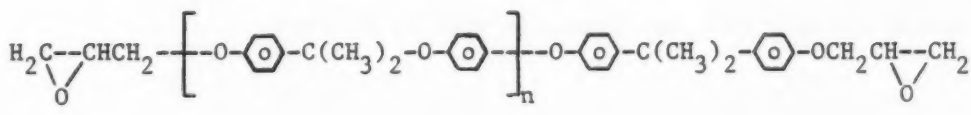
Chlorohydrin Intermediate Sodium hydroxide



Ether with Terminal Epoxy Groups Sodium chloride Water (B)



Ether with Terminal Epoxy Groups Bisphenol A



Epoxy Resin (C)

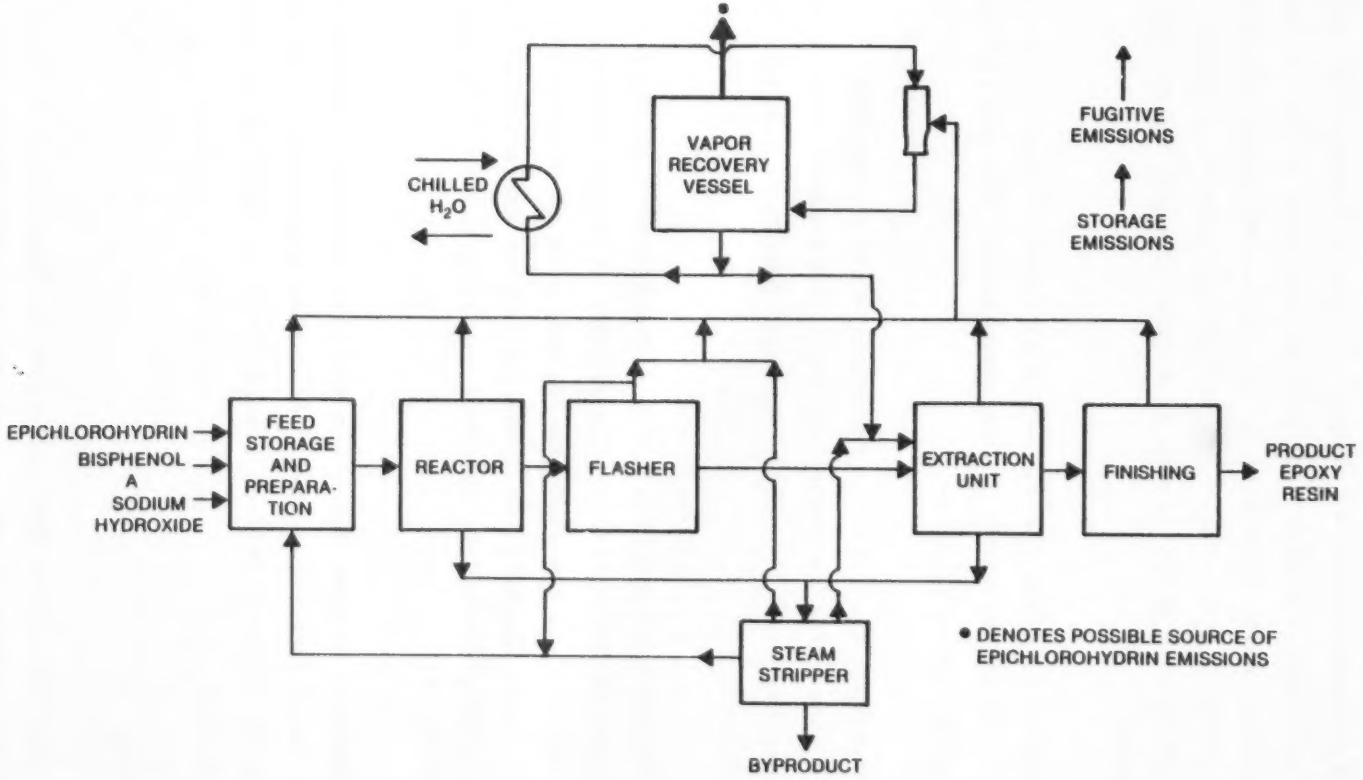


Figure 3. Basic operations that may be used in the continuous production of epoxy resins from epichlorohydrin (well-controlled facility).

Whether the above reaction sequence applies to all manufacture of epoxy resins from epichlorohydrin and bisphenol A is not known. One company mentions the addition of acetone and sodium carbonate to the reactor along with the epichlorohydrin, bisphenol A and sodium hydroxide raw materials.[7] The acetone serves as a solvent. The purpose of sodium carbonate is not known. Toluene, methyl ethyl ketone or methyl isobutyl ketone may also be used as solvents.[6]

The following is a description of epoxy resin production by one manufacturer.[7] It is not known how representative this description is of the industry; no other was available.

The resin solution product is concentrated in an atmospheric flasher, then extracted with water to remove residual by-product. Finishing involves vacuum flashing, high-vacuum evaporation, and polish filtration with diatomaceous earth.

Water from the extraction section, combined with the aqueous byproduct from the reactor, is steam stripped to recover volatile organics. These organics are recycled to the feed preparation area along with the overheads from the atmospheric flasher. Overhead water from the steam stripper is combined with makeup water from the vent recovery system to be used as solvent by the extraction unit.

The atmospheric flasher and steam stripper share an overhead system vented to the vapor recovery system. All other equipment in the extraction section either is operated full of liquid (with no vent) or is connected to the overhead system.

Emission Factors

For the well controlled facility shown in Figure 3, the vapor recovery vessel is the only source of process emissions. One company reports

98 percent control efficiency for the vapor recovery system and epichlorohydrin emissions of 0.005 g/kg of product from this vent.[7] There is virtually no chance for upset emissions of epichlorohydrin from this process.[8] Data on epichlorohydrin process emissions from an uncontrolled facility were not available.

Fugitive emissions from pumps, valves, flanges, etc. account for almost 88 percent of the total epichlorohydrin emissions from epoxy resin production.[9] Fugitive emissions of epichlorohydrin are minimized because of its high flammability and toxicity. At least one company leak-proofs with pressurized double seal systems all pumps which handle epichlorohydrin.[8] The dominance of fugitive emissions is due in part to the controls in place on other emission sources.

Several techniques are used in the industry for control of emissions from storage and handling:

- Maintain storage tanks at constant level and high pressure relief setting;
- Vent storage tanks to the vapor recovery system;
- Vent storage tanks to a balloon header which breathes in and out;
- Use floating roof tanks;
- Control emissions from operational abnormalities and refilling after maintenance with a thermal oxidizer; and
- Vent emissions to carbon adsorption unit if balloon system becomes overpressured.

One plant estimates epichlorohydrin storage emissions of 0.3 g/kg (control methods used not given). This same company predicts no epichlorohydrin storage emissions when storage tanks are vented to a balloon header. A carbon adsorption unit is used if the balloon system becomes overpressured.[8] As an industry average, storage emissions account for less than 4 percent of all epichlorohydrin emissions from epoxy resin manufacture.[9]

Source Locations

As of 1983, only two companies were producing epoxy resins from epichlorohydrin in a continuous process: Shell Oil Company, Deer Park, TX, and Dow Chemical Company, Freeport, TX. Shell Oil also produces epoxy resins by a batch process. Shell's resin is known as EPON®, while Dow's is known as D.E.R.®

PRODUCTION OF EPOXY RESINS AND OTHER PRODUCTS FROM EPICHLOROHYDRIN (BATCH PROCESS)

A number of products are made from epichlorohydrin by batch processes because the amounts involved are small. Among these are various epoxy resins, phenoxy resins, polyamine and polyaminoamide (wet-strength) resins, glycidyl ether (a surfactant), and elastomers.

The epichlorohydrin is usually almost totally consumed in the reaction; therefore, process vents are not a major source of emissions. For this reason and because process data are scarce, the following discussion focuses on the epichlorohydrin feed facilities.

Process Description

The industry practices described below are compiled from data collected from several producers.[10] A general flow diagram for batch production of epoxy resins is shown in Figure 4 while a probable flowsheet for epichlorohydrin elastomer is illustrated in Figure 5.

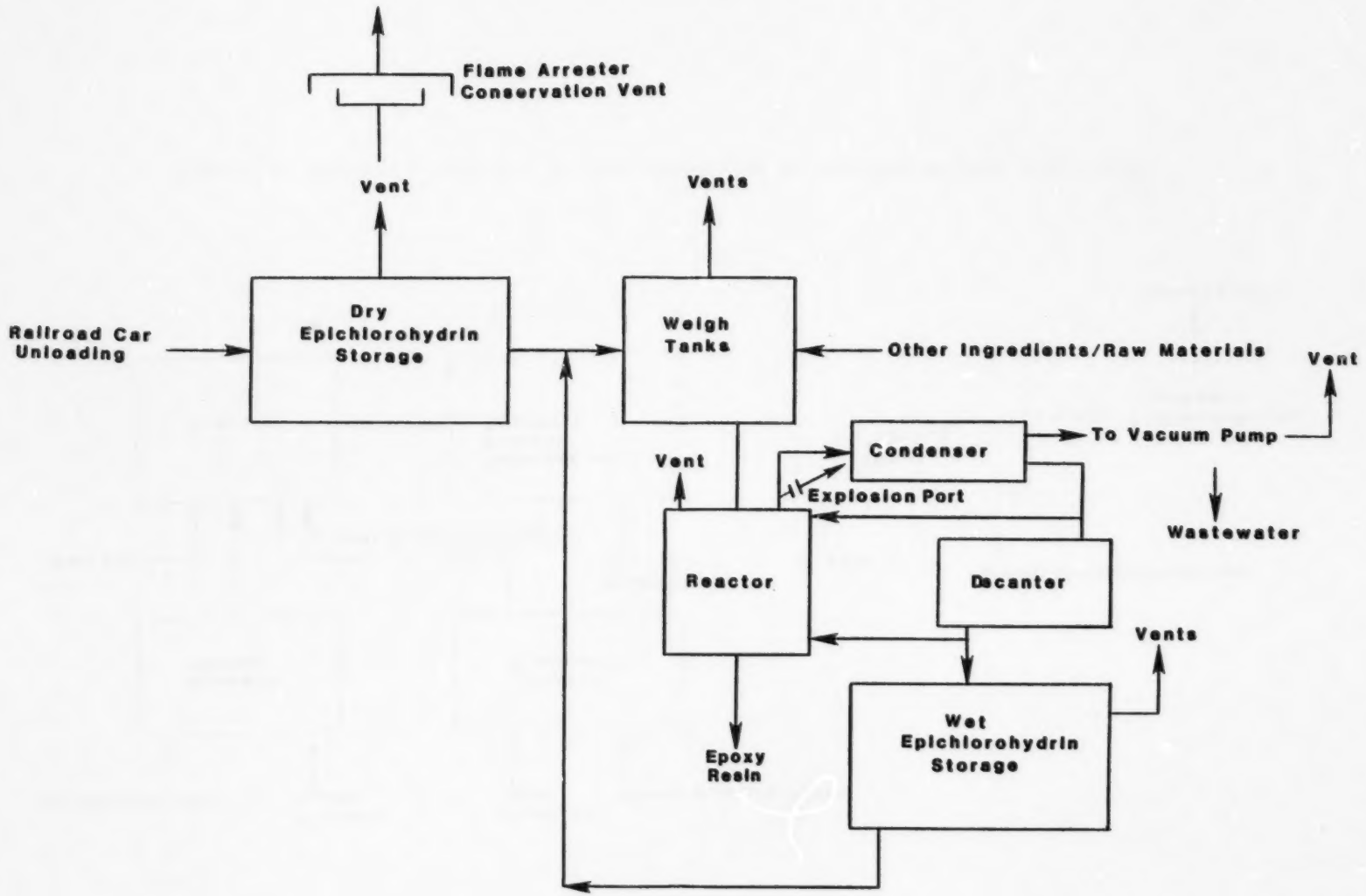


Figure 4. Flow diagram for the batch production of epoxy resins.[11]

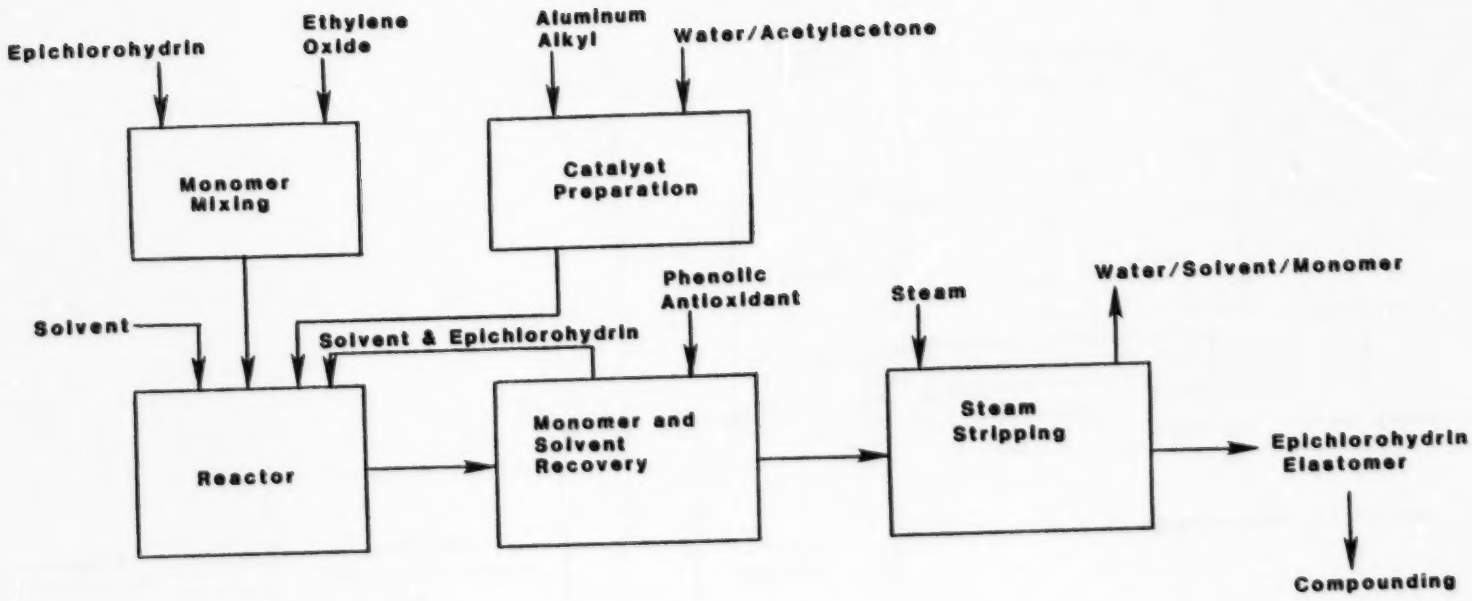


Figure 5. General flowsheet for the production of epichlorohydrin elastomers.[1]

Epichlorohydrin is commonly supplied to the facilities by railcar, then transferred to a storage tank. It may then be transferred to a weigh tank, to a blend tank, or directly to the reactor. Transfer is normally via closed pipeline and sometimes under nitrogen blanket, although it may simply be drawn from drums by vacuum.

The number of process sources of epichlorohydrin emissions varies widely. The reactor vent is the primary--and often the only--process source. This vent may be uncontrolled or it may be controlled by vent condenser, packed tower scrubber, incinerator, pressure vacuum vent valve, or other device. Several producers report epichlorohydrin emissions from this vent only while the reactor is being charged; others report more continuous emissions. Epichlorohydrin content in process streams can be reduced to less than 1 percent after the reactor.

Only one epoxy resin manufacturer, as shown in Figure 4, provides for the handling of epichlorohydrin stripped from the product: this epichlorohydrin is stripped from the product by vacuum distillation and stored in "wet" tanks for reuse. Epichlorohydrin in the "wet" tanks is covered by a layer of water, which is eventually removed through an overflow weir, mixed with alkaline wastewaters (which hydrolizes the epichlorohydrin) in a covered surge tank, and released to the sewer. The epichlorohydrin is recycled to the weigh tanks.

Other possible process sources for epichlorohydrin emissions include transfer of the reaction mixture to another vessel and product refinement. These sources are typically very minor.

Epichlorohydrin emissions are also associated with feed storage and handling. Breathing losses are caused by expansion and contraction of the vapors within the storage vessel. Working losses are associated with the filling and emptying of the vessel. Fixed roof tanks are standard for storage of the epichlorohydrin feed, though one plant used closed head drums.

Emissions from the tanks may be controlled by nitrogen blanket, water blanket, or pressure-vacuum vent valve. As mentioned above, epichlorohydrin is normally transferred via pipeline or under nitrogen blanket. Epichlorohydrin is drawn from the drums by vacuum.

Fugitive sources may account for much of the epichlorohydrin emissions from these processes. Some producers have no system for controlling leaks from pumps, compressors, flanges, valves, and sample connections. In some plants, the vacuum pumps in epichlorohydrin service are equipped with liquid seals which serve to reduce epichlorohydrin vapor discharges. Two producers report no fugitive emissions of epichlorohydrin. One attributes this absence of emissions to the control measures used, including sealed magnetic drives on all pumps which transfer epichlorohydrin. The other, a producer of polyamide resins, attributes it to a negative pressure (3.92 in Hg. abs.) within the process. At this negative pressure, any leakage would be into the process from the atmosphere.

Wastewater and solid waste streams containing epichlorohydrin may be associated with these processes. No analyses are available for epichlorohydrin emissions from these sources. However, because epichlorohydrin is readily hydrolized, emissions are presumed to be minimal.

Emission Factors

Table 7 presents epichlorohydrin emission factors for batch processes which use epichlorohydrin as a feedstock. These emission factors were calculated from emission and throughput totals for the polyamide resin, elastomer, and surfactant industries and are only broad averages, not representative of any particular facilities.

Fugitive emissions are by far the largest category of epichlorohydrin emissions from these industries, constituting 87 percent of the total emissions from this sector. As indicated in Section 3, fugitive emissions may

TABLE 7. EMISSION FACTORS FOR THE RELEASE OF EPICHLOROHYDRIN FROM BATCH PROCESSES WHICH USE EPICHLOROHYDRIN AS A FEEDSTOCK

Source	Emission Factor[a] (g/kg)	% Total Emissions
Process Vents	0.56	7
Storage Facilities[b]	0.47	6
Fugitive Sources[c]	7.10	87
TOTAL	8.13	100

[a]Grams of epichlorohydrin emitted per kilogram of epichlorohydrin used. Calculated from aggregate emission and throughput totals for various resin, elastomer, and surfactant producers which use epichlorohydrin as a raw material in batch processes, as given in References 9 and 12. These factors do not represent the emission rates at any particular facilities.

[b]Includes storage tanks and transfer operations.

[c]Includes pump seals, compressors, flanges, valves, pressure relief devices, sample connections and open-ended lines. Calculations are based on the use of average VOC fugitive emission factors for SOCMI process components representing emissions from relatively uncontrolled facilities where no significant leak detection and repair programs are in place for fugitive emission control and were extrapolated to an average plant schedule of 300 days per year. Because epichlorohydrin does not flow continuously through process components in batch processes, these factors may be overstated. Also, some manufacturers use various measures to detect and reduce fugitive emissions. Some use personal monitors on employees and perform regular area monitoring. One manufacturer uses sealed magnetic drives on pumps in epichlorohydrin service while another maintains the process system at negative pressure so all leaks from pumps, flanges, etc. are vented back to the process. No estimates are available of the effectiveness of these measures.[10]

dominate not necessarily because they are large, but because other sources are fewer and/or well-controlled. Also, the fugitive emission factors given in Table 7 may be overstated because they do not account for the fact that in batch processes the epichlorohydrin is not flowing continuously through process components.[9]

Source Locations

Table 8 gives the names and locations of some producers of epoxy resins (batch), polyamide-epichlorohydrin resins, epichlorohydrin elastomers, and surfactants made from epichlorohydrin. No claim of completeness is made for this table.

TABLE 8. SOME PRODUCERS OF EPICHLOROHYDRIN PRODUCTS[9,13]

Product-Company	Location
Epoxy Resins (Batch Process)	
Celanese Corporation	Louisville, KY
Ciba-Geigy Corporation	Tom's River, NJ[a]
Union Carbide Corporation	Bound Brook, NJ
Shell Oil Company	Deer Park, TX
Polyamide-Epichlorohydrin Resins	
Borden	Demopolis, AL Sheboygan, WI
Diamond Shamrock	Charlotte, NC
Hercules	Chicopee, MA Hattiesburg, MS Milwaukee, WI Portland, OR Savannah, GA
Georgia-Pacific	Peachtree City, GA Eugene, OR
Rohm and Haas	Philadelphia, PA
Epichlorohydrin Elastomers	
Hercules	Hattiesburg, MS
B.F. Goodrich	Avon Lake, OH
Surfactants	
Proctor & Gamble	Cincinnati, OH Kansas City, KS
Flame Retardents	
Stauffer Chemical	Gallipolis Ferry, WV

[a]Ciba-Geigy has announced plans to close this facility and add 45Gg (100 million lbs) of capacity to its McIntosh, AL, facility.[1]

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of epichlorohydrin emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contact with plant personnel.

REFERENCES FOR SECTION 5

1. Assessment of Epichlorohydrin Uses, Occupational Exposure, and Releases. Dynamac Corporation, Rockville, MD. Prepared for the Office of Toxic Substances, U. S. Environmental Protection Agency, Washington, D.C. Prepared under EPA Contract No. 68-02-3952. July, 1984.

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3. Syracuse Research Corporation. Investigation of Selected Potential Environmental Contaminants: Epichlorohydrin and Epibromohydrin. (Prepared for U. S. Environmental Protection Agency, PB80-197585). Syracuse, NY. March, 1980.

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7. Texas Air Control Board. Permit Applications for Shell Chemical Company, Deer Park, TX. Austin, TX.

8. Texas Air Control Board. Permit Applications for Dow Chemical Company, Freeport, TX. Austin, TX.

9. Memorandum entitled "Epichlorohydrin Emissions Summary: Epichlorohydrin Source Assessment" from Jeffrey A. Shular, Midwest Research Institute, Raleigh, NC, to David Beck, EPA, Research Triangle Park, NC. February 16, 1984.

10. Nonconfidential portions of letters submitted to J. R. Farmer, Emission Standards and Engineering Division, Office of Air Quality Planning and Standards, U. S. EPA, Research Triangle Park, NC, by industrial users of epichlorohydrin. October - December 1983.

11. Letter from H. H. Flegenheimer, Celanese Corporation, Louisville, KY, to Dave Beck, U. S. EPA, Research Triangle Park, NC. January 6, 1984.

12. Memorandum entitled "Calculations of Gas Velocities and Storage and Fugitive Emissions: Epichlorohydrin Source Assessment" from Jack R. Butler and Jeff Shular, Midwest Research Institute, Raleigh, NC, to David Beck, U. S. EPA, Research Triangle Park, NC. February 17, 1984.

13. SRI International. 1985 Directory of Chemical Producers - United States. Menlo Park, CA. 1985.

SECTION 6

EMISSIONS FROM THE USE OF EPICHLOROHYDRIN-CONTAINING PRODUCTS

Trace levels of epichlorohydrin residues may be contained in products manufactured from epichlorohydrin feedstocks. During the use of these products, volatilization of the epichlorohydrin is possible under certain temperature and pressure conditions, thereby resulting in potential atmospheric emissions of epichlorohydrin. The potential for such emissions is discussed in this section in connection with the use of epoxy resins, glycerin, elastomers, and wet-strength resins.

USE OF EPOXY RESINS

Epichlorohydrin residue levels in epoxy resins have been determined from resin manufacturers through the use of product technical bulletins and material safety data sheets. A Shell Oil Company technical bulletin on its epoxy resins and reactive diluents (produced from epichlorohydrin) indicates that trace levels of epichlorohydrin are contained in these products.[1] Many EPON® resins are sold under manufacturer's product specifications that the epichlorohydrin content cannot be greater than 5 ppm (by weight).[1,2] Shell has indicated that epichlorohydrin levels in most EPON® resins are generally in the 1 ppm - 2 ppm range.[1,2] However, specialty resins and reactive diluents do exist that have epichlorohydrin levels ranging from 10 ppm - 1,400 ppm.[1]

One manufacturer has empirically determined the vapor concentrations of epichlorohydrin above epoxy resins that would result from the exposure of epichlorohydrin-containing resins to air under various temperature conditions. These experimental results are shown in Table 9. As expected, the higher the

TABLE 9. EPICHLOROHYDRIN VAPOR CONCENTRATIONS ABOVE EPOXY RESINS AT VARIOUS TEMPERATURES UNDER STATIC EQUILIBRIUM CONDITIONS[1]

	Epichlorohydrin Levels in the Resin, ppm, wt.		
	10	5	1
Temperature, °C (°F)	Epichlorohydrin Level in Vapor, ppm, v/v		
27 (80)	0.6	0.3	0.06
49 (120)	2	1	0.2
NOTE: 60°C (140°F) Recommended Handling Temperature			
71 (160)	5	2.6	0.5
93 (200)[a]	12	6	1.2
116 (240)	26	13	2.6
138 (280)	50	23	5.0
149 (300)	64	32	6.4

[a]93°C (200°F) is the maximum recommended handling temperature.

temperature during use, the higher the potential for epichlorohydrin emissions. It should be noted that these experiments gave results indicating that the epichlorohydrin concentrations potentially occurring are independent of the method of application (i.e., pouring, spreading, or spraying) of the resin. Epichlorohydrin air concentrations were found, however, to be dependent on the surface area of resin in contact with air.

Several verifications have been made in industrial situations of epichlorohydrin emissions from the use of epoxy resins. In one case, structural steel members were being coated with an epoxy paint by hand spraying. Measured epichlorohydrin concentrations in air in the building where spraying was occurring ranged from 2.4 mg/m^3 - 138.9 mg/m^3. In several OSHA tests of industrial processes involving epoxy resins for plastics production and processing, epichlorohydrin concentrations of 0.01 ppm - 3.8 ppm were measured in workplace air.[1] These examples indicate the potential for epichlorohydrin emissions from epoxy resins that contain epichlorohydrin residues.

USE OF SYNTHETIC GLYCERIN

Epichlorohydrin residues in glycerin have been determined to be very low and thus the potential for epichlorohydrin emissions from volatilization during glycerin use is practically nonexistent. Dow Chemical has tested its synthetic glycerin products and found no epichlorohydrin residues (detection limit of 1.5 ppm).[1,3] Epichlorohydrin residues in synthetic glycerin are minimal or nonexistent because any residual epichlorohydrin is hydrolyzed during the production process. In addition, several high temperature distillations are performed to purify crude synthetic glycerin that are very effective at eliminating any potential residues such as epichlorohydrin. Theoretical yield calculations involving the chemical reactions taking place during synthetic glycerin production have been performed to estimate potential epichlorohydrin residue levels. These calculations give an estimate of epichlorohydrin levels in synthetic glycerin of less than 1 part per trillion.[1]

USE OF WET-STRENGTH RESINS

Although quantitative data on the levels of epichlorohydrin contained in wet-strength resins could not be identified in the literature, some amount of epichlorohydrin residue is projected to occur in aqueous wet-strength resin solutions.[1] If epichlorohydrin is contained as a contaminant in the resins, it would most likely be released as a vapor during application of the resin to paper and during paper manufacture dewatering and drying steps. No workplace or other epichlorohydrin emissions data related to wet-strength resin use could be found.

USE OF ELASTOMERS

The potential for epichlorohydrin residues to be found in crude epichlorohydrin elastomers is significant because they are prepared with an excess of epichlorohydrin. However, the reaction of the residual epichlorohydrin with vulcanizing agents and stabilizer additives and the adsorption of residual epichlorohydrin by carbon black filler help prevent excessive releases of epichlorohydrin during elastomer storage and use. No quantitative data on epichlorohydrin residue levels in epichlorohydrin elastomers could be found in the literature.

Tests of workplace air at elastomer processing plants have not detected any epichlorohydrin. Tested process areas included elastomer weighing stations, elastomer extrusion, two-roll mill mixing, and molding.[1,4]

REFERENCES FOR SECTION 6

1. Assessment of Epichlorohydrin Uses, Occupational Exposure, and Releases. Dynamac Corporation, Rockville, Maryland. Prepared for the Office of Toxic Substances, U. S. Environmental Protection Agency, Washington, DC. Prepared under EPA Contract No. 68-02-3952. July 1984.

2. Shell Oil Company. Shell Chemical Company Technical Bulletin SC: 106-82:7-15. 1982. Houston, Texas.

3. Letter from Arnold, S., Dow Chemical to Parris, G., Dynamac Corporation. January 1984. Information on Dow's synthetic glycerin.

4. Hercules Chemical. Herclor® Epichlorohydrin Elastomers, Hazards Associated with Epichlorohydrin Monomer in the Handling and Processing of Herclor® Elastomers. Hercules Bulletin ORH-24D. 1983.

SECTION 7

SOURCE TEST PROCEDURES

EPA is investigating source sampling and analytical procedures for epichlorohydrin air emissions, but none have yet been published or recommended. The sampling and analysis methods presented in this chapter for epichlorohydrin emissions represent those that have been published in the literature as viable methods. The presentation of these methods in this report does not constitute endorsement or recommendation, nor does it signify that the contents necessarily reflect the views and policies of the U.S. EPA.

LITERATURE REVIEW OF SAMPLING METHODS

Adsorption onto activated charcoal is a preferred sampling method for epichlorohydrin. Silica gel has also been used as the adsorbent.[1] The National Institute for Occupational Safety and Health (NIOSH) method number S118 for epichlorohydrin prescribes the use of standard commercial tubes containing 150 g of 20/40 mesh activated carbon in two sections: 100 g in the front section and 50 g in the rear. The two sections are divided by 2 mm of polyethylene foam. Samples as large as 20 liters collected at 200 ml/min are allowed. The epichlorohydrin is desorbed from the charcoal with carbon disulfide. Water vapor interferes with sample collection by displacing the organic vapors.[3]

Impingers or bubblers containing distilled water or dilute sulfuric acid have also been used to collect epichlorohydrin vapors. In one method, a 2-liter sample is drawn through two bubblers in series at a rate of 0.5 liter/minute. Each bubbler contains 8 milliliters of water. During one

test with about 5.2 ppm epichlorohydrin the efficiency of the first bubbler was 80 percent. The efficiency of the second bubbler was not given.[1]

Plastic bags, glass bottles, aluminum foil-polyester laminate bags and teflon bags have been used with varying rates of success as collection devices. Sampling duration is usually from a few seconds to two minutes. In one test in which the epichlorohydrin concentration ranged from 5 to 27 ppm, samples in teflon bags suffered a 20 to 26 percent loss of epichlorohydrin after 24 hours. Samples in aluminum foil-polyester bags suffered a 19 to 40 percent loss under the same conditions.[1]

LITERATURE REVIEW OF ANALYTICAL METHODS

Gas chromatography has become the method of choice for separation and analysis of organic materials because it is sensitive, specific, and suitable for analysis of samples collected on charcoal.[1] The National Institute for Occupational Safety and Health (NIOSH) method for determination of epichlorohydrin calls for a flame ionization detector and a column packed with 10 percent carbon disulfide. The overall NIOSH method operates over the concentration range 11.7 to 43.1 mg/m^3 with a relative error of 0.7 percent at 5 ppm.[2] Any other compound with the same retention time as epichlorohydrin will interfere, but the interference can be eliminated by changing the separation conditions.[3]

Colorimetry is the most common wet method for determination of epichlorohydrin concentration. Several methods involve hydrolysis of the epichlorohydrin to glycol, then oxidation to formaldehyde. For aqueous solutions of epichlorohydrin, both hydrolysis and oxidation are usually accomplished with periodic acid. If the sample was collected in dilute sulfuric acid, hydrolysis is accomplished by the sulfuric acid and periodic acid is added for oxidation. The formaldehyde may be reacted with sodium arsenite or ammonia and acetylacetone reagent, Schiff's reagent, or phenylhydrazine and potassium ferricyanide to form colored complexes. The

sodium arsenite/acetylacetone method can detect as little as 20 μg epichlorohydrin. The Schiff's reagent method can detect 0.01 to 0.1 mg epichlorohydrin in a 6-ml solution. The phenylhydrazine/potassium ferricyanide method has been used for epichlorohydrin concentrations of from 0.45 to 14 mg/m^3 in air with maximum error of 0.3 percent.[1] The ammonia/acetylacetone method can detect as little as 6 ppm epichlorohydrin with an error of about 2 percent.[2] Formaldehyde or any substance which could yield formaldehyde, such as ethylene oxide or ethylene glycol, will interfere with these methods. Many aldehydes will interfere with the Schiff's reagent method.[1]

Practical and detailed methods for quantitative determination of epichlorohydrin concentrations with infrared spectroscopy have not been developed. One source indicates a minimum detection limit of 3000 ppm.[1] Another source indicates measurement of 10 ppm with ± 2 percent precision and accuracy. Terminal olefins can interfere.[2]

Advanced techniques have been applied to qualitative, rather than quantitative, determination of epichlorohydrin. For example, photoelectron spectroscopy can distinguish among epichlorohydrin, epibromohydrin, epifluorohydrin, and other halo-oxygen compounds. It is not suitable for quantitative determinations.[2]

REFERENCES FOR SECTION 7

1. National Institute for Occupational Safety and Health (NIOSH). Criteria for a Recommended Standard. Occupational Exposure to Epichlorohydrin. U. S. Department of Health, Education and Welfare. (No date.)

2. Syracuse Research Corporation. Investigation of Selected Potential Environmental Contaminants: Epichlorohydrin and Epibromohydrin. (Prepared for U. S. Environmental Protection Agency, PB80-197585). Syracuse, NY. March 1980.

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